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Lattice vibrations of glasses

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Abstract

Measurements of the thermal conductivity of glasses have led to a model of their lattice vibrations. They are not described as waves, as they are in crystals, but as uncorrelated harmonic motions of individual atoms. The lattice vibrations of fully cerammed, crystalline glass ceramics have been found to be either waves, as in crystals, or vibrations of individual atoms, as in glasses. The understanding of the cause for this different behavior has been aided by studies of systematically doped crystals.

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Keywords: Glasses; Thermal conductivity

1. Introduction

For nearly a century now, the lattice vibrations of crystalline solids have been successfully described with elastic waves traveling through the crystal with the speed of sound, in a correlated motion of neighboring atoms. This model is due to Born and von Kármán [1], and to Debye [2]. Chemical disorder in nearly perfect crystals leads to a modification of these waves in the vicinity of the defects, to so-called impurity modes, without, however, affecting the wave nature of the lattice vibrations. In amorphous solids or glasses, however, measurements of the thermal conductivity at temperatures above 50 K are better described with a different model, due to Einstein [3], in which the harmonic motion of neighboring atoms are uncorrelated. This model provides a very simple phenomenological description of their lattice vibrations in the frequency regime of terahertz, and allows a quantitative description of the heat transport in these solids, although a theoretical understanding is still lacking. The same model has also been successful in describing the lattice vibrations of some fully cerammed glass ceramics, but not in others. Efforts to understand the cause for this difference have led to the study of simple, systematically disordered crystals. The experimental situation will be briefly reviewed here.

2. Thermal conductivity of glasses: Einstein's model

The thermal conductivity of dielectric solids depends on whether they are crystalline or amorphous, as shown for SiO_2 in Fig. 1. In the crystalline phase, it increases rapidly with decreasing temperatures, goes through a maximum, and then decreases. In the amorphous phase, it decreases with decreasing temperatures at all temperatures. In crystals, the heat is carried by elastic waves. The probability for the collision of their quanta in inelastic collisions by Umklapp processes decreases with decreasing temperatures, which leads to the increase of the thermal conductivity, even though the number density of the heat carrying phonons decreases. The maximum of the thermal conductivity is reached when the phonon mean free path becomes comparable to the crystal dimension. At the lowest temperatures, the conductivity varies as the third power of the temperature, as determined by the specific heat of the heat carrying waves in the crystal. In glasses, the very different thermal conductivity cannot be described with elastic

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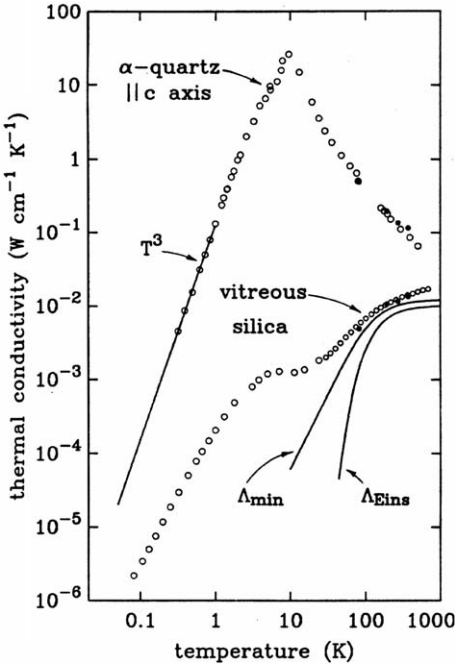

Fig. 1. Characteristic difference of the thermal conductivity of a solid, here SiO_2, in the crystalline (top) and the amorphous phase (bottom). Λ_{Eins} is the thermal conductivity based on Einstein's model, using a single Einstein oscillator frequency. $\Lambda_{\min}$ is based on Eq. (1). It fits the measurements well above ~50 K. Ref. [4].

waves that are being scattered, at least not above temperatures above 50 K. Instead, it can be remarkably well described with a model in which the heat is transmitted in a random walk from one atom to its nearest and next-nearest neighbors, with a jump time equal to half a period of their oscillation. This was shown by Cahill et al. [4,5], using a slight modification of a model proposed by Einstein [3] as he attempted – with no success – to describe the experimental data obtained on crystals. His model is based on the assumption of entirely uncorrelated harmonic oscillators, the Einstein oscillators. Since their frequency had to be determined from low temperature specific heat measurements, and since Einstein's model of the specific heat describes the latter only approximately, as is now known, the determination of an Einstein frequency from these measurements is somewhat uncertain, and so is the thermal conductivity Λ_{Eins} derived from this model. In order to circumvent the resulting arbitrariness, Cahill modified Einstein's model to contain a distribution of such frequencies, with each of these modes containing as many atoms as are contained in half a wavelength of a Debye wave. The energy was then exchanged between these extended oscillating domains of equal sizes, in the same way as it is between the 26 oscillators in Einstein's original model. With this modification, the somewhat uncertain Einstein frequency was replaced by a Debye cut-off frequency, which can be determined with much less arbitrariness from measurements of the low temperature speeds of sound v_i and from the known number density n of the atoms in the glass. This leads to the following expression for the thermal conductivity $\Lambda_{\min}$:

$$\Lambda_{\min} = \left(\frac{\pi}{6}\right)^{1/3} k_{\mathrm{B}} n^{2/3} \sum_i v_i \left(\frac{T}{\Theta_i}\right)^2 \int_0^{\Theta_i/T} \frac{x^3 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2} \mathrm{d}x \qquad (1)$$

The sum is taken over the three sound modes (two transverse and one longitudinal); Θ_i is the (Debye) cut-off frequency for each polarization expressed in degrees K, $\Theta_i = v_i(\hbar/k_{\mathrm{B}})(6\pi^2 n)^{1/3}$, and $x = \Theta_i/T$. As shown in Fig. 1, the result fits the data for a-SiO_2 even better than Λ_{Eins} at temperatures above 50 K. The most significant difference, however, is that all quantities appearing in this equation are unambiguously known. The discrepancy between the model conductivity and the experimental data which increases rapidly as the temperature is decreased below 50 K results from long wavelength elastic waves which become important as carriers of heat at these temperatures. Below 10 K, the mean free path of these phonons increases rapidly. They are being scattered by the tunneling states, which are another part of the low energy lattice vibrations of glasses which will, however, not be discussed here. For a recent review, see Ref. [6].

A remarkable experimental fact is that the thermal conductivities of all amorphous solids measured so far are similar, as shown in Fig. 2, and that they lie in a band only a little larger than one order of magnitude, as shown for the data below 1 K with the two dashed lines separated by a double arrow varying as T^2.

$\Lambda_{\min}$ as given by Eq. (1) has been shown to fit the experimental data remarkably well quantitatively for all 14 glasses measured to-date. As an illustration, the measured thermal conductivity has been compared with the one predicted by the model at 300 K in Fig. 3, where the dashed line indicates the perfect fit (a-Al_2O_3 from Ref. [7], a–C from Ref. [8]; all other data as reviewed in Ref. [9]). Note

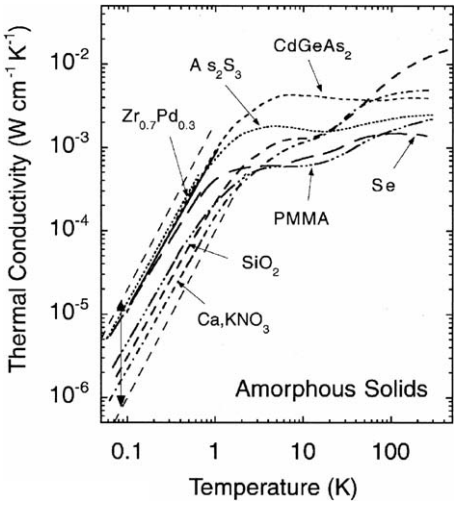

Fig. 2. The thermal conductivity of all amorphous solids is remarkably similar in both temperature dependence and magnitude. The two straight dashed lines drawn below 1 K differ by less than a factor of 20. They vary as the temperature squared Ref. [6].

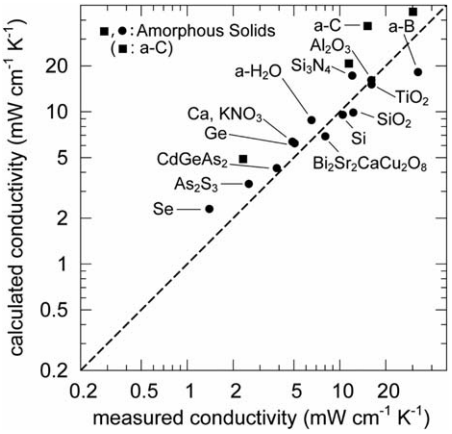

Fig. 3. Comparison of the values of the thermal conductivity calculated based on Einstein's model, $\Lambda_{\min}$, see Eq. (1), with those measured on amorphous solids. For a–C (solid squares), films with four different densities and elastic constants were compared with the model at 400 K [8], for all other amorphous solids the comparison was made at 300 K [7,9]. The dashed line indicates perfect agreement between theory and experiment.

that for amorphous carbon four films with different elastic constants and number densities have been measured (the solid squares, measured at 400 K). The agreement with the predicted values is very good, considering that no adjustable parameters were used.

It should be emphasized that in spite of the remarkable agreement with the experimental results, the theoretical basis for this model, i.e., the assumption of fully uncorrelated harmonic oscillators, is by no means firmly established at this point. Theoretically better founded calculations of the thermal conductivity of amorphous solids have been performed [10–13]. They do, however, suffer from their complexity, evidenced by the fact that so far, they have only been performed for silicon and germanium. The beauty of Einstein's model is the fact that it is extremely simple, and appears to describe the experimental facts remarkably well. Based on the experimental evidence, it may be fair to conclude that the model predicts the thermal conductivity of amorphous solids above $\sim$50 K, based solely on their speeds of sound and their number densities. One word of caution is in order, though: if molecular vibrations are not thermally excited at room temperature, as for example hydrogen bonds in organic polymers, then the total number density to be used in Einstein's model should be smaller than the total number density of atoms in the solid, which leads to ambiguity (see also later, in Fig. 7, where the model is applied to fullerenes). For that reason, organic polymers have not be included in this review. See, however, Ref. [4] for PMMA.

3. Thermal conductivity of glass ceramics and disordered crystals

So far, the distinction of the lattice vibrations of crystalline and amorphous solids on the basis of their thermal conductivity has appeared to be very simple, as illustrated in Fig. 1. In order to show this difference most dramatically, Stephens studied a lithium aluminosilicate glass ceramic, Corning Code 9623 [14]. It was not available in the amorphous phase, but based on numerous other measurements of other silicate glasses, its thermal conductivity in the glass phase could be considered to be well known. The sample Stephens measured had been crystallized by heat treatment, and was therefore expected to have a larger thermal conductivity, like that of a crystal, perhaps somewhat decreased below that of a perfect crystal because of defect scattering. However, much to his surprise, the crystallization had not led to any significant change of the thermal conductivity, instead, it continued to be exactly like that of a glass! This is shown in Fig. 4 with some recent measurements taken over a wider temperature range[15]. This puzzling result became even more mysterious when another glass ceramic, Corning Code 9606, a magnesium aluminosilicate, behaved exactly as had been previously expected by us, see Fig. 5, also taken from Ref. [15]: Ceramming did raise its thermal conductivity, at high tem-

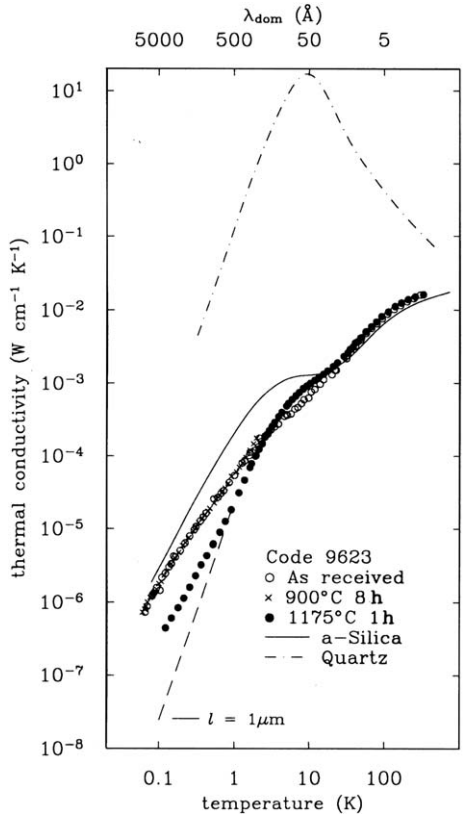

Fig. 4. Thermal conductivity of the Corning glass ceramic Code 9623 after two stages of annealing (ceramming). After the second anneal, the crystallite sizes were of the order of 1–2 μm, yet the thermal conductivity above 10 K remains identical to that of a-silica (the solid curve). Dash-dot curve: crystalline SiO_2 (quartz). Dashed line: thermal conductivity (Casimir effect) for a phonon wavelength-independent mean free path $l = 1$ μm. The agreement with the 1175 °C annealed sample (solid circles) provides further evidence that at low temperatures the heat is carried by waves. Their dominant wavelength λ_{dom}, i.e., the wavelength of the phonons which carry most of the heat at a given temperature, is shown on the upper scale. Ref. [15].

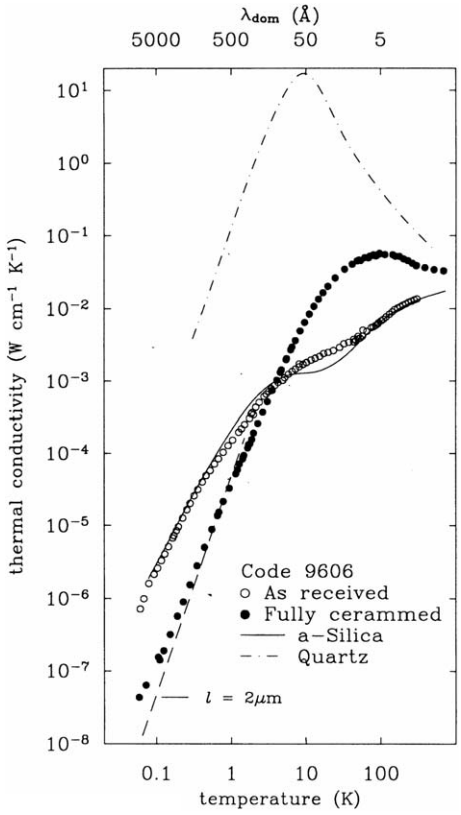

Fig. 5. Thermal conductivity of the Corning glass ceramic Code 9606 in the fully amorphous form (open circles), and after complete ceramming, leading to crystallite sizes in the range of 1–3 μm (solid circles). The three drawn curves have the same meaning as in Fig. 4. Ref. [15].

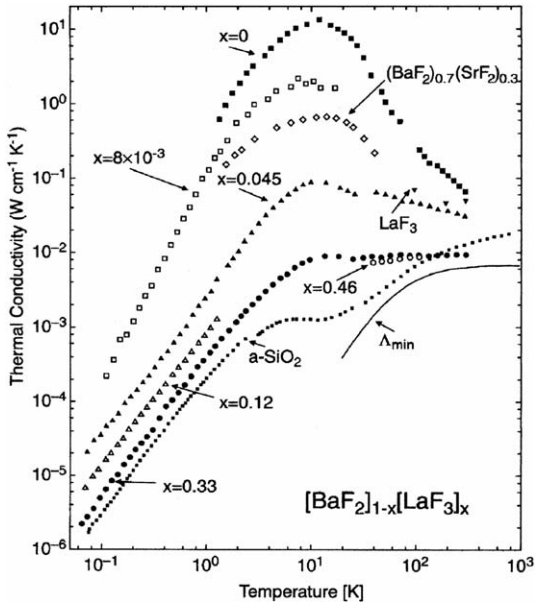

Fig. 6. Thermal conductivity of $(BaF_2)_{1-x}(LaF_3)_x$ [5,6]. The pure BaF_2 ($x = 0$) has a thermal conductivity typical of perfect crystals. The addition of LaF_3 leads to a thermal conductivity approaching that of an amorphous solid (a-SiO_2) for large x. Note that the conductivities for $x = 0.33$ and $x = 0.46$ are very close, approaching the minimum thermal conductivity calculated for these crystals at high temperatures. The addition of a large concentration of (divalent) SrF_2 to the BaF_2 has a relatively small effect. A glasslike thermal conductivity is not reached.

peratures approaching that of quartz. Thus, the lattice vibrations of fully cerammed, crystalline glass ceramics could either be like those of a glass, or of a crystal, although both of them are highly complex in composition and crystal structure. How could this difference come about? And what could this difference possibly tell us about the origin of the oscillations in amorphous solids?

These questions led to the investigation of systematically disordered crystals. An example is shown in Fig. 6, taken from Ref. [6]: When divalent SrF_2 is added to divalent BaF_2, the Sr ions replace the Ba ions, and the resulting disorder leads to defect scattering (open diamonds) even at very large concentrations. The elastic excitations remain those of a crystal. The Sr ions act pretty much like isotopic phonon scatterers (another example with similar results are mixed crystals of KCl and KBr [5]). However, the addition of trivalent lanthanum to the BaF_2 leads to the incorporation of fluorine ions on interstitial sites, and now the thermal conductivity approaches that of amorphous solids as the concentration x of the La increases, as shown with the comparison with amorphous silica and with Λ_{min} obtained with Eq. (1) from the measured speeds of sound and the known number density of atoms in the mixed crystal for $x = 0.33$ (Table 1 in Ref. [5]). Pure LaF_3 (inverted triangles) again has a conductivity close to that of an (imperfect) crystal. The incorporation of interstitial F^--ions will cause local stresses. It may therefore be concluded that random stresses in the crystal may play an important role in creating the lattice vibrations resembling those of amorphous solids. Random stresses can also be expected in the Code 9623 glass ceramic. In the fully cerammed sample, the major crystal phase is β-spodumene in which a fraction of the interstitial sites will be filled with positive lithium and magnesium ions. In the cerammed Code 9606, the major crystalline phase is cordierite, in which the Mg-ions occupy a regular array of lattice sites. Interstitial ions are absent [15]. This led us to the suggestion that interstitial ions in the 9623, causing random stresses, result in a thermal conductivity of a glass, while without such interstitials, as in the 9606, the thermal conductivity is like that of a crystal, in which the heat is carried by waves.

The close correlation between random stress fields in crystals and lattice vibrations of glasses has now been observed in a number of disordered crystals. For a review, see Refs. [6,15]. As an illustration, Fig. 7 shows with the open circles the comparison of the observed thermal conductivity in these solids at 300 K with that predicted by the Einstein model, Eq. (1). These data have been taken from Ref. [9]. They have been shown together with the data points (solid circles) for amorphous solids in Fig. 3. It is important to emphasize that in no disordered dielectric crystal thermal conductivities smaller than those of its amorphous phase have been observed, or briefly: no open circle data have been found to the left of the dashed line in Fig. 7. This is the experimental justification for calling

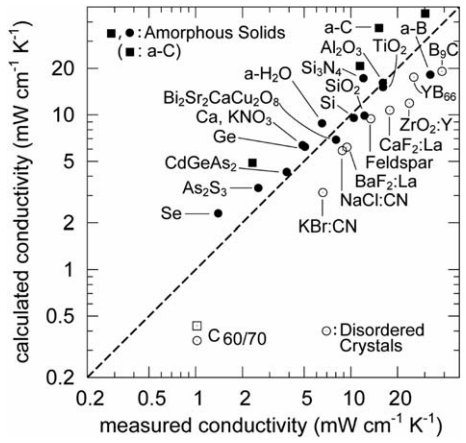

Fig. 7. Comparison of the thermal conductivity $\Lambda_{\min}$ calculated from Eq. (1) at 300 K for crystals with glasslike lattice vibrations with the values measured at the same temperature (Ref. [9]). The solid circles are the same as shown in Fig. 3 (for amorphous samples). For all crystals shown, excepting the compacted polycrystalline fullerene sample, the existence of random stresses is to be expected. For the fullerene points, the buckyballs have been assumed to be rigid, i.e., the number density n_i has been assumed to be that of the buckyballs. The open square has been calculated with the original Einstein model of the thermal conductivity, using only a single oscillator frequency, since the specific heat measurements allowed the determination of such a frequency without ambiguity [17].

the thermal conductivity $\Lambda_{\min}$. given by Eq. (1) the 'minimum thermal conductivity'. One other point needs to be emphasized: While in numerous crystals random stresses have been identified as the potential cause for glasslike behavior of the thermal conductivity, it is premature to conclude from this that random stresses are the only cause. For example, Cohn et al. [16] have identified a glasslike thermal conductivity observed in the clathrate crystal $Sr_8Ga_{18}Ge_{30}$, and have associated its origin with a rattling motion of the Sr^{2+} in its cage.

4. Conclusion

The amazing observation that crystallized (cerammed) glass ceramics of different chemical composition can have remarkably different thermal conductivities, resembling either those of a crystal or of a glass, has found an explanation through the study of systematically doped crystals. Random stresses appear to play an important role in creating the glasslike behavior. However, in how far this finding may also explain the lattice vibrations in structurally amorphous solids, tempting as this explanation may be, must still be considered to be an open question.

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